

УДК 541.124+546.431

Wu Ze, PhD student (BSTU);

L. A. Bashkirov, D. Sc. (Chemistry), professor (BSTU);

S. V. Slonskaya, PhD (Chemistry), assistant professor (BSATU);

S. V. Trukhanov, senior researcher (Materials Science SPC of Belarus NAS);

L. S. Lobanovskiy, senior researcher (Materials Science SPC of Belarus NAS);

A. I. Galyas, senior researcher (Materials Science SPC of Belarus NAS)

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF HIGHLY-COERCIVE $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ FERRITES

High-coercivity ferrite samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ ($x = 0; 0.1; 0.2; 0.3; 0.4; 0.5$) with magnetoplumbite structure were prepared from oxides Fe_2O_3 , Gd_2O_3 , ZnO and carbonate SrCO_3 by solid-state ceramic method, the dependence of the unit cell parameters a and c on the value of x was determined. XRD showed that the samples with $x \geq 0.1$ were not single-phase, and the samples with $x \geq 0.2$ contained not only bases phase with the structure of magnetoplumbite, but also the $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ phases. It was found that increase of the x value leads to a slight decrease in the Curie temperature (from 727 K for the basic ferrite $\text{SrFe}_{12}\text{O}_{19}$ to 714 K for $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ solid solution with $x = 0.5$). It has been found that at 300 K values of spontaneous magnetization (n_0) and coercive force (σH_c) of solid solution $\text{Sr}_{0.9}\text{Gd}_{0.1}\text{Fe}_{11.9}\text{Zn}_{0.1}\text{O}_{19}$ are respectively 1.3 and 2.3% higher than for the base ferrite $\text{SrFe}_{12}\text{O}_{19}$, and values of samples with $x > 0.1$ of these magnetic properties decreases gradually.

Introduction. Ferrites $\text{BaFe}_{12}\text{O}_{19}$, $\text{SrFe}_{12}\text{O}_{19}$ with the structure of the magnetoplumbite mineral are uniaxial ferrimagnetics. They have a large value of the coercive force (H_c), good chemical stability, low cost and are widely used for the manufacture of permanent magnets [1–3]. Until the end of the last century, the improvement of the magnetic properties of permanent magnets of ferrites $\text{BaFe}_{12}\text{O}_{19}$, $\text{SrFe}_{12}\text{O}_{19}$ were mainly achieved by modifying their production technology. Carrying out of such works made it possible to raise energy product $(BH)_{\max}$ of anisotropic permanent ceramic magnets to a value of 35 kJ/m^3 , but this value is much less than theoretically possible. Further progress in the improvement of the quality of the permanent magnets from barium and strontium ferrites can be obviously expected not only by modifying their production technology (this destination is almost exhausted), but also due to purposeful, scientific and well founded changes of solid solutions composition based on barium and strontium ferrites with magnetoplumbite structure.

Until now promising direction in the search of new magnetic materials is the study of solid solutions based on $\text{SrFe}_{12}\text{O}_{19}$, in which ions Sr^{2+} are partially substituted by ions of rare earth elements Ln^{3+} ($\text{Ln} - \text{La}, \text{Nd}, \text{Pr}, \text{Sm}$), and an equivalent amount of Fe^{3+} ions is substituted by ions M^{2+} ($\text{M} - \text{Zn}, \text{Co}, \text{Mn}$) [4–10]. In the present work the synthesis of ferrites $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ ($x = 0; 0.1; 0.2; 0.3; 0.4; 0.5$) with the structure of magnetoplumbite and their crystal structure, Curie temperature, the saturation magnetization and coercive force are studied.

Experimental procedure. Ceramic ferrite samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ ($x = 0; 0.1; 0.2; 0.3; 0.4; 0.5$) are synthesized by solid phase method from gadolinium oxide (Gd_2O_3), iron (Fe_2O_3), zinc

(ZnO) and strontium carbonate (SrCO_3). All reagents were qualified (analytical grade). Mixing and grinding of the starting materials, taken in a desired ratio, were carried out in a planetary mill Pulverizette 6 of Fritsch firms adding ethanol. The resulting charge (with the addition of ethanol to improve the compressibility) was compressed under a pressure of 50–75 MPa into tablets with a diameter of 19 mm and a height of 5–7 mm, which were then dried in air at 373 K and calcined on substrates of alumina at a temperature of 1473 K in air for 8 hours. After pre-firing the tablets were crushed and milled. Tablets having a diameter of 9 mm, a height of 3.2 mm and the bars having a size of $5 \times 5 \times 30 \text{ mm}^3$ were pressed and calcined at 1473 K for 4 hours in air. X-ray diffraction diagrams of ferrite samples were recorded on a Bruker D8 X-ray diffractometer (radiation CuK_α) at room temperature. Lattice parameters were calculated using the X-ray table processor RTP. Dependence of the magnetization on the temperature and magnetic field value of ferrites $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ was obtained in NAS scientific and practical center of materials science. Specific magnetization (σ_{ud}) of ferrite powder in a magnetic field of 8.6 kE was measured by the Faraday method in the temperature range of 77–900 K. The specific saturation magnetization and hysteresis loop parameters of specific magnetization of ferrite samples of cylindrical shape of 5.0–5.4 mm length and a diameter of 1–1.2 mm were measured by vibrating method in the magnet field up to 14 Tl at temperatures of 5 and 300 K.

Results and their discussion. The analysis of X-ray diffraction diagrams (Fig. 1) showed that the sample of ferrite $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ with $x = 0$ was a single phase with the structure of magnetoplumbite; samples with $x \geq 0.1$, besides the main phase with

the structure of magnetoplumbite also contained $\alpha\text{-Fe}_2\text{O}_3$ phase, the number of which gradually increased as x increased to 0.5; in the samples with $x \geq 0.2$ gadolinium ferrite phase $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ was present.

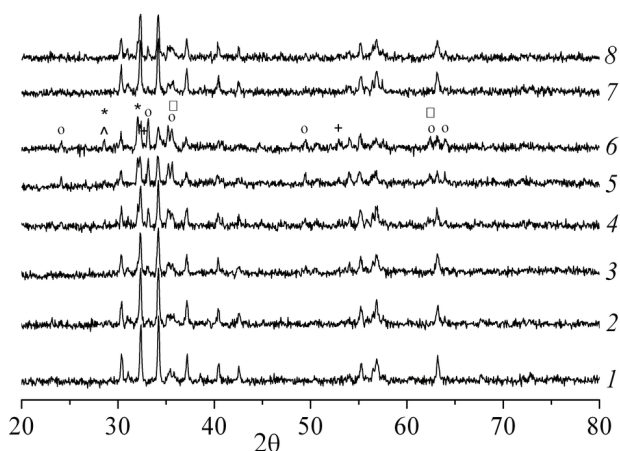


Fig. 1. X-ray diffraction diagrams of ferrite samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$; $x = 0$ (1); 0.1 (2); 0.2 (3); 0.3 (4); 0.4 (5); 0.5 (6), and samples with $x = 0.1$ (7); 0.2 (8), additionally calcined at 1473 K:
o – $\alpha\text{-Fe}_2\text{O}_3$, * – $\text{Gd}_3\text{Fe}_5\text{O}_{12}$,
+ – $\text{GdFeO}_3\text{-ZnFe}_2\text{O}_4$, ^ – Gd_2O_3

In samples with $x \geq 0.3$ phases ZnFe_2O_4 and GdFeO_3 were present; in the samples with $x = 0.4, 0.5$ – Gd_2O_3 phase was present. It could be assumed that the presence of admixture phases in these samples is due to the incompleteness of solid phase reactions. Therefore multiphase samples of ferrites $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ with $x = 0.1, 0.2$ were milled, pressed into pellets and further calcined in air at 1473 K for 4 hours. X-ray-phase analysis of these further fired samples showed that in the sample of ferrite $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ with $x = 0.1$ phase content $\alpha\text{-Fe}_2\text{O}_3$ decreased, but it does not fully disappeared. Diffraction diagram of the sample with $x = 0.2$, was virtually unchanged. This shows that the limit value of the degree of substitution x of ions $\text{Sr}^{2+}, \text{Fe}^{3+}$ by ions $\text{Gd}^{3+}, \text{Zn}^{2+}$ in ferrite $\text{SrFe}_{12}\text{O}_{19}$ at 1473 K is slightly less than 0.1. Table 1 shows the values of the lattice parameters a, c and the unit cell volume V of the ferrite samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$. It can be seen that the increase of the degree of substitution x from 0 to 0.1 leads to reduction of the lattice parameters a and c from the quantities 5.8838, 23.046 Å for $\text{SrFe}_{12}\text{O}_{19}$ to 5.8818, 23.033 Å, and with a further increase in the degree of substitution x to 0.5 lattice parameters a and c change without a definite regularity.

The results of the values of the lattice parameters a, c and volume V for $\text{SrFe}_{12}\text{O}_{19}$ obtained in the present study differ slightly from published data [11] for this ferrite ($a = 5.8844$ Å, $c = 23.05$ Å, $V = 691.20$ Å³).

Table 1
The values of the lattice parameters a, c and V of $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ ferrites with the structure of magnetoplumbite

x	$a, \text{Å}$	$c, \text{Å}$	$V, \text{Å}^3$
0	5.8838	23.046	689.957
0.1	5.8818	23.033	690.059
0.2	5.8849	23.058	691.563
0.3	5.8837	23.053	691.121
0.4	5.8833	23.093	692.223
0.5	5.8831	23.092	692.161

Photos of the cleavage surface of ferrite samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$, obtained with a scanning electron microscope JEOL JSM-5610V (Japan), are shown in Fig. 2. The photographs show that most of the crystallites (grains) do not have a good cut and their size is of 1.5–4.0 microns.

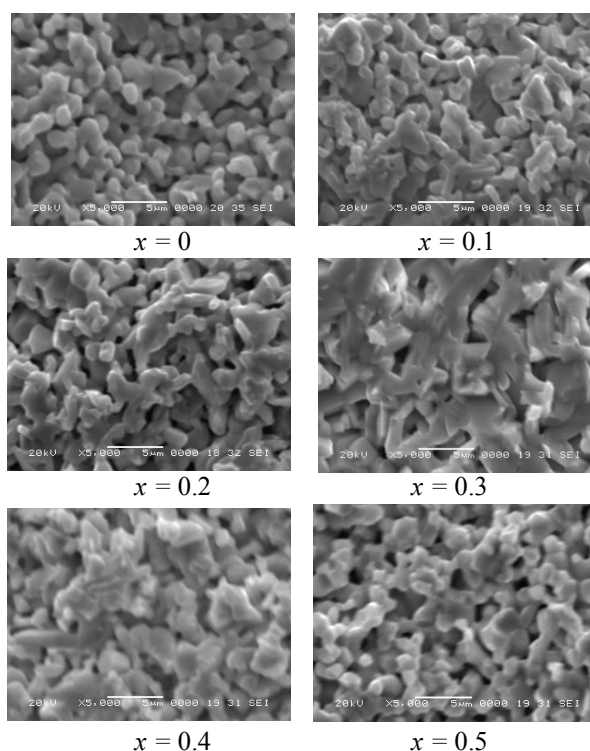


Fig. 2. Electron micrographs of ferrites $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ system, $\times 5.000$ times magnification

Figure 3 shows the temperature dependences of the specific magnetization (σ_{sp}) measured by the Faraday method in a magnetic field of 0.86 T in the temperature range of 77–900 K for the studied samples of ferrites $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$. It allowed to determine the Curie temperature (T_c) of these ferrites, the values of which are given in Table 2.

It is found that an increase of the parameter x of samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ leads to a slight decrease of the Curie temperature from 727 K for $\text{SrFe}_{12}\text{O}_{19}$ to 714 K for the ferrite with $x = 0.5$.

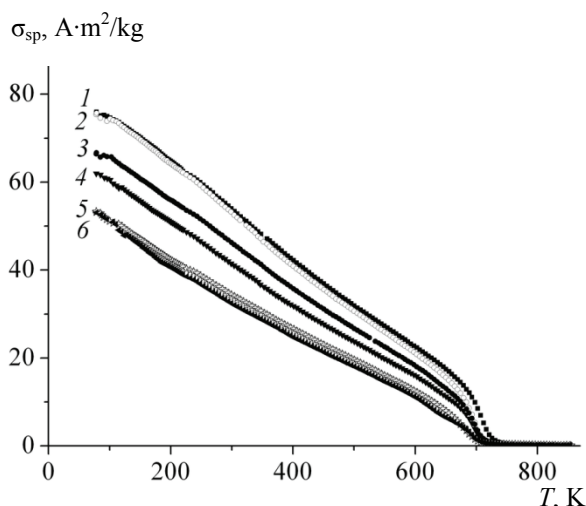


Fig. 3. Temperature dependences of the specific magnetization σ_{sp} of ferrite samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ at x : 1 – 0; 2 – 0.1; 3 – 0.2; 4 – 0.3; 5 – 0.4; 6 – 0.5

Figure 4 gives an example of the magnetization hysteresis loop for $\text{SrFe}_{12}\text{O}_{19}$ at 5 K. It is seen that the saturation magnetization of the ferrite is achieved in the fields of about 3 T, above which there is a slight increase of the hysteresis-free magnetization due to the paraprocess.

Such magnetic hysteresis loop of the specific magnetization at temperatures of 5 and 300 K in magnetic fields up to 14 T is obtained for other samples of ferrites $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ ($0 < x \leq 0.5$). However, in Fig. 5 for the sake of clarity, they are shown in magnetic fields only up to 3 T, i. e. without the part of linear dependence σ_{sp} from H , but which are present in the range of magnetic fields 3–14 T in all experimentally obtained magnetic hysteresis loops of the investigated ferrites.

By extrapolating the linear part of the σ_{sp} from H to $H = 0$ T for $\text{SrFe}_{12}\text{O}_{19}$ (Fig. 4) and for all other investigated ferrites at temperatures of 5 and 300 K, the values of specific spontaneous magnetization (σ_0), which values are given in Table 2 are de-

termined. For ferrite samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ with $x = 0; 0.1$ according to the formula

$$n_0 = \frac{\sigma_0 M}{5585},$$

where M – molar mass of corresponding ferrite, 5585 – quantity equal to the product of the Bohr magneton (μ_B) per Avogadro number, the calculated value of the spontaneous magnetization (n_0), expressed in Bohr magnetons per one formula ferrite unit (Table 2).

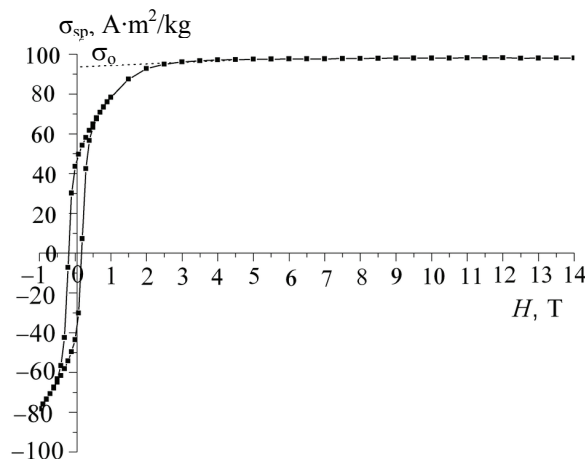


Fig. 4. The hysteresis loop of the specific magnetization at 5 K for $\text{SrFe}_{12}\text{O}_{19}$

For the value of specific saturation magnetization (σ_s) of the corresponding ferrite was taken the value of specific magnetization measured in a magnetic field of 3 T. The data presented in Table 2 show that σ_s values for all investigated ferrites are only slightly less than the values σ_0 . Values n_0 of one formula ferrite unit $\text{Sr}_{0.9}\text{Gd}_{0.1}\text{Fe}_{11.9}\text{Zn}_{0.1}\text{O}_{19}$ at 5 and 300 K are respectively higher than for the base $\text{SrFe}_{12}\text{O}_{19}$ ferrite per 1.7 and 1.3%. However, with further increase of the degree of substitution from 0.2 to 0.5, a decrease of spontaneous magnetization value n_0 and σ_s is observed.

Table 2
The Curie temperature (T_c), the specific spontaneous magnetization (σ_0), the specific saturation magnetization (σ_s), the spontaneous magnetization of one formula unit (n_0), specific residual magnetization (σ_r), coercive force (σH_c) of ferrite samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ at 5 and 300 K

x	T_c , K	$T = 5$ K					$T = 300$ K				
		σ_s , $\text{A}\cdot\text{m}^2/\text{kg}$	n_s , μ_B	σ_{sp} , $\text{A}\cdot\text{m}^2/\text{kg}$	σ_r , $\text{A}\cdot\text{m}^2/\text{kg}$	σH_c , kA/m	n_s , μ_B	σ_s , $\text{A}\cdot\text{m}^2/\text{kg}$	σ_r , $\text{A}\cdot\text{m}^2/\text{kg}$	σH_c , kA/m	
0	727	97.05	18.45	96.13	43.55	143.64	12.69	66.21	32.33	259.14	
0.1	718	97.95	18.76	96.71	42.44	118.02	12.85	67.08	32.97	265.21	
0.2	717	88.45		87.88	35.13	105.56		57.58	27.57	238.04	
0.3	716	86.62		86.61	27.62	83.11		50.54	21.12	214.46	
0.4	716	76.34		76.28	22.01	59.08		43.95	19.35	174.88	
0.5	714	74.71		74.53	16.35	53.99		42.27	18.82	174.26	

It can be noted that the solid solution of ferrite $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ with $x = 0.1$ at 300 K has a value of spontaneous magnetization n_0 and that of coercive force σH_c is more than ferrite $\text{SrFe}_{12}\text{O}_{19}$ has up to 1.3 and 2.3% respectively. Such increase at 300 K of spontaneous magnetization and coercive force substituting ions Sr^{2+} , Fe^{3+} by ions Gd^{3+} , Zn^{2+} in the ferrite $\text{SrFe}_{12}\text{O}_{19}$ up to $x = 0.1$ should lead to an increase of energy product $(\text{BH})_{\text{max}}$ of the permanent magnets at 300 K manufactured of a solid solution $\text{Sr}_{0.9}\text{Gd}_{0.1}\text{Fe}_{11.9}\text{Zn}_{0.1}\text{O}_{19}$. However, as x increases from 0.1 to 0.5 we observe a gradual decrease of the values of the coercive force σH_c at 5 and 300 K (see Table 2) and the coercive force σH_c at 5 and 300 K for the sample with $x = 0.2$ is less than for $\text{SrFe}_{12}\text{O}_{19}$. For all the studied ferrites the temperature rise from 5 to 300 K results in a significant increase of the coercive force (Table 2).

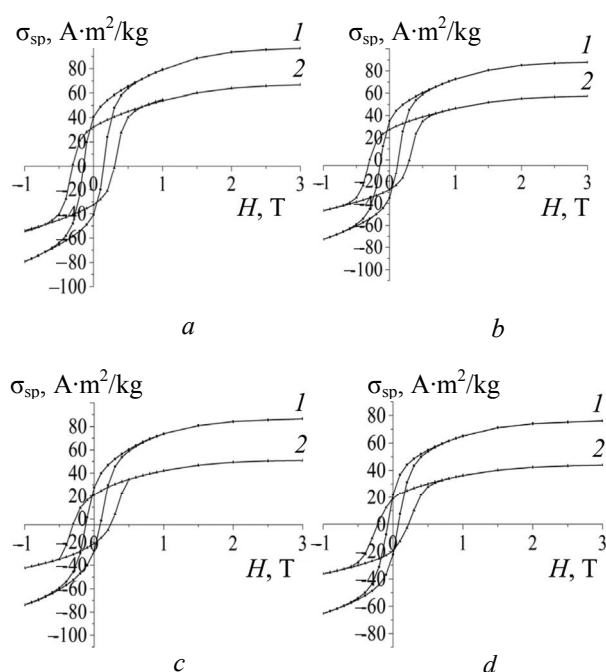


Fig. 5. Hysteresis loops of specific σ_{sp} magnetization at 5 K (1) and 300 K (2) for $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ when $x = 0.1$ (a), $x = 0.2$ (b), $x = 0.3$ (c), $x = 0.4$ (d)

Conclusion. Samples of ferrites $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ ($x = 0; 0.1; 0.2; 0.3; 0.4; 0.5$) were prepared by solid phase method. X-ray phase analysis showed that the samples with $x \geq 0.1$ were multiphase. Samples with $x \geq 0.2$ except main solid solution phase of ferrites $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ with magnetoplumbite structure contained admixture phases $\alpha\text{-Fe}_2\text{O}_3$, $\text{Gd}_3\text{Fe}_5\text{O}_{12}$. It was found that an increase of the parameter x of ferrite samples $\text{Sr}_{1-x}\text{Gd}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ leads to a slight decrease of the Curie temperature of from 727 K for

$\text{SrFe}_{12}\text{O}_{19}$ to 714 K for the ferrite with $x = 0.5$. It was found that the solid solution of ferrite $\text{Sr}_{0.9}\text{Gd}_{0.1}\text{Fe}_{11.9}\text{Zn}_{0.1}\text{O}_{19}$ at 300 K has a value of spontaneous magnetization n_0 and coercive force σH_c more than ferrite $\text{SrFe}_{12}\text{O}_{19}$ on 1.3 and 2.3%, respectively. Such increase at 300 K of the spontaneous magnetization of the coercive force of $\text{Sr}_{0.9}\text{Gd}_{0.1}\text{Fe}_{11.9}\text{Zn}_{0.1}\text{O}_{19}$ solid solution should lead to an increase of energy product $(\text{BH})_{\text{max}}$ of the permanent magnets manufactured from this solid solution.

References

- Смит Я., Вейн Ч., Ферриты. Физические свойства и практическое применение. М., 1962. 504 с.
- Технология производства материалов магнитоэлектроники / Л. М. Летьок [и др.]. М.: Металлургия, 1994. 416 с.
- Крупичка С. Физика ферритов и родственных им магнитных окислов. В 3 т. М.: Мир, 1976. Т. 2. 504 с.
- High Energy Ferrite Magnets / H. Taguchi [et al.] // 7th International Conference on Ferrites, Bordeaux, 3–6 september 1996 / Bordeaux Convention Center France. Bordeaux, 1996. P. 3–4.
- Yamamoto H., Obara G. Magnetic properties of anisotropic sintered magnets using Sr–La–Co system powders by mechanical compounding method // J. of the Japan Society of Powder and Powder Metallurgy. 2000. Vol. 47. P. 796–800.
- Substitution effects in M-type hexaferrite powders investigated by Mossbauer spectrometry / L. Lechevallier [et al.] // J. of Magnetism and Magnetic Materials. 2005. Vol. 290–291. Iss. 2. P. e1237–e1239.
- Influence of the presence of Co on the rare earth solubility in M-type hexaferrite powders / L. Lechevallier [et al.] // J. of Magnetism and Magnetic Materials. 2007. Vol. 316. Iss. 2. P. e109–e111.
- On the solubility of rare earths in M-type $\text{SrFe}_{12}\text{O}_{19}$ hexaferrite compounds / L. Lechevallier [et al.] // J. of Phys: Condens. Matter. 2008. Vol. 20. P. 175203–175212.
- Кристаллическая структура и магнитные свойства высококоэрцитивных твердых растворов $\text{Sr}_{1-x}\text{Pr}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ / Д. Д. Полько [и др.] // Неорганические материалы. 2011. Т. 47, № 1. С. 81–86.
- Crystal structure and magnetic properties of $\text{Sr}_{1-x}\text{Sm}_x\text{Fe}_{12-x}\text{Co}_x\text{O}_{19}$ solid solutions / Wu Ze [et al.] // Inorganic Materials. 2014. Vol. 50, No. 3. P. 285–290.
- Powder Diffraction File. Swarthmore: Joint Committee on Powder Diffraction Standard Card № 84–1531.

Received 03.03.2014